

PATENT SPECIFICATION

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(54) PIGMENTS USEFUL IN ELECTROPHOTOGRAPHY

(71) We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America of 343 State Street, Rochester, New York 14650, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to pigments useful in electrophotography.

According to the present invention there is provided a process for the formation of a pigment comprising the steps of reacting in an aqueous medium an acidic dye (or a salt thereof) which is water-soluble and has an acidity such that a saturated aqueous solution thereof has a pH less than 5, with a basic dye (or a salt thereof) which is also water-soluble and has a basicity such that a saturated aqueous solution thereof has a pH greater than 8, so as to form a precipitate and then treating the precipitate with an acidic mordant.

The pH values described herein and in the appended claims are measured at 20°C.

The pigments produced by the process of the present invention are useful in electro-photographic developers and have high tintorial power which can be produced in a wide variety of hues. In addition, they are resistant to fading, and are suitable for application by either dry or liquid development techniques. The acidic dyes which are used in preparing the pigment preferably contain at least two sulphonic or carboxylic acid radicals. The basic dyes which are used in preparing the pigments preferably contain at least two amino, including substituted amino, radicals. Substituents on the amino radicals can be an alkyl group having from 1 to 8 carbon atoms and which can be a straight chain or branched chain alkyl group, e.g., methyl, ethyl, isopropyl, hexyl, octyl or 2,2,4-trimethylpentyl or an aryl group, e.g., phenyl or

naphthyl including aryl groups bearing such alkyl substituents as defined above, amino, including substituted amino, nitro or halogen, an aralkyl group, e.g., methylphenyl, benzyl or dimethylnaphthyl. The dyes can be used in the form of their acidic salts. Thus, the acid dyes may be used in the form of salts of alkali metals, such as sodium, potassium and lithium, and the basic dyes may be used in the form of hydrohalides, sulphates or nitrates. When the acidic and basic dyes described above react, each dye acts as a precipitant for the other, and a highly insoluble pigment results.

The acidic and basic dyes used as the starting materials for preparing the pigments of the present invention can be chosen from a wide variety of known dye classes. For example, dyes selected from the following classes are useful: nitro, azo, including disazo, arylmethane, including di- and tri-aryl methane, methine, acridine, thiazole, azine, anthraquinone and phthalocyanine. These and other useful classes of dyes can be found in the Preamble to the Colour Index, Volume 3, Second Edition, 1956.

Particular acidic dyes which are illustrative of the many useful dyes include the following:

4 - (4,8 - disulfonaphthyl - 2 - azo) - 3 - methyl - 1 - (4 - sulfophenyl) - 5 - pyrazolone; 4 - (2,5 - dichloro - 4 - sulfophenylazo) - 3 - phenyl - 1 - (4 - sulfophenyl) - 5 - pyrazolone; 1 - carboethoxy - 3 - methyl - 6 - (4' - chloro - 2' - sulfoanilino) - 2 - oxo - 2,3 - dihydrobenzanthrone, sodium salt; 5,5' - ureylenebis[2 - (2 - amino - 6 - sulfo - 8 - hydroxy - 1 - naphthylazo)benzenesulfonic acid], tetrasodium salt, C.I. 25380; 3,3' - [4,4' - ureylenebis(2 - methylphenyl-azo)]bis(1,5 - benzenedisulfonic acid), tetrasodium salt, C.I. 29025;

[Price 25p]

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5 - [2 - anilino - 4 - [4 - (3 - carboxy - 4 - hydroxyphenylazo) - anilino] - 5 - triazin - 2 - ylaminol] - 4 - hydroxy - 3 - [4 - (8 - hydroxy - 3,6 - disulfo - 1 - naphthylazo) - 2 - methoxy - 3 - methylphenylazo] - 2,7 - naphthalenedi-sulfonic acid, pentasodium salt, C.I. 34045; 6,6' - ureylenebis{2 - [4 - (2,4 - dichloro - 6 - sulfophenylazo) - 3 - methylphenylazo] - 1 - naphthol - 3 - sulfonic acid}, tetrasodium salt, C.I. 35785; and anhydro - 3,6 - bis(diethylamino) - 9 - (2,4 - disulfophenyl) - xanthylium hydroxide, sodium salt, C.I. 45100.

Dyes such as these are sold under various names, including the following:

Brilliant Alizarine Light Red B, Sandoz, Ltd.

20 Solantine Pink 4BL, C.I. 25380
Solantine Yellow RL, C.I. 29025
Pontamine Fast Green G, C.I. 34045
Sirius Rubine 6B, C.I. 35785
Xylene Red B, C.I. 45100
25 Solophenyl Fast Blue Green BL, C.I. Direct Green 27

Similarly, many basic dyes can be used, including the following illustrative materials:

30 9 - o - carboxyphenyl - 3,6 - bis(diethylamino)xanthylium chloride, C.I. 45170; 1,1',3,3,3',3' - hexamethylindocarbocyanine chloride, C.I. 48070; bis [3,7 - bis(dimethylamino)phenazathionium]tetrachlorozincate, C.I. 52015; and 35 bis(3 - amino - 7 - dimethylamino - 2 - methylphenazathionium)tetrachlorozincate, C.I. 52040.

Dyes such as these are sold under various names, including the following:

40 Rhodamine B, C.I. 45170
Astraphloxine FF, C.I. 48070
Methylene Blue BX, C.I. 52015
Toluidine Blue, C.I. 52040
45 Genacryl Yellow 5GF, C.I. Basic Yellow 13
Genacryl Yellow 2RL, C.I. Basic Yellow 25

50 Usually, acidic and basic dyes which have approximately the same hue are selected to react with each other, although other combinations may be desirable or even preferred for a given use. For example, it may be desired to modify the hue of a cyan dye slightly by reacting it with a green dye, in order to achieve a better color balance in a given dye set. Similarly, it may be necessary to shift the color of a magenta dye slightly. This can be accomplished by reacting it with a red or a blue dye without sacrificing covering power.

55 60 Of course, neutrals can be produced by mutual precipitation of dyes of less pure color, such as, for example, precipitation of an impure cyan with an impure magenta to produce a dark brown or a black.

65 Pigments are typically prepared in accord-

ance with the present invention by dissolving a quantity of the acidic dye in a first portion of hot water. A slight molar excess of the basic dye is then dissolved in a second portion of hot water. The solution of the basic dye is then slowly added to the solution of the acidic dye, with rapid stirring, producing a thick slurry. When almost enough of the basic dye solution has been added to completely precipitate the acidic dye, a drop of the slurry is spotted on filter paper. A deposit of pigment appears at the point of contact, the water moving away from this point in a circle. If the water is colored uniformly, an excess of one dye is indicated. The deposit on the paper is observed under 365 nm. mercury illumination. Absence of fluorescence indicates incomplete precipitation, i.e., an excess of acidic dye, as in general acidic dyes do not fluoresce under these conditions whereas basic dyes do fluoresce. Addition of the solution of basic dye is then continued slowly, and removed samples are examined chromatographically as above at intervals, until the circle of water first becomes colorless and then becomes colored again. A monitoring of the appearance of the circle under ultraviolet illumination as before shows a weak fluorescence, indicating a slight excess of basic dye. When the end point, as thus determined, is reached, the stirring is continued for 15 to 20 minutes, during which time the slurry is allowed to cool. Stirring is stopped and cooling continued until the mixture reaches about room temperature (20°C). The slurry is then filtered and pressed dry on a Büchner funnel. The resulting dried cake is stirred up in a quantity of cold water for 10 to 20 minutes to remove unreacted dye, and filtered again. It is then stirred up in a quantity of hot ethyl acetate, filtered, extracted with cold ethyl acetate, and washed down on the filter with a quantity of acetone. Finally, the cake is dried on a steam bath.

In preparing certain of the pigments of the invention, it may be desirable to add other materials to the slurry before the initial drying. In order to facilitate the filtering step, it may be desirable, for example, to add a sodium salt such as sodium chloride, sodium sulfate or sodium acetate. This effect, well known in the pigment-making art as "salting-out", improves particle size so the filter paper does not become plugged by an excess of extremely fine particles.

To produce the pigments of the present invention, the precipitate formed by reaction of the acidic dye with the basic dye is treated with an acid mordant. This is most conveniently accomplished by adding the acidic mordant to the stirred slurry before drying. Acidic mordants which are particularly effective for this purpose are phosphotungstic acid, phosphomolybdic acid, and mixtures of phosphotungstic acid with phosphomolybdic acid.

Treatment of the precipitate with these acidic mordants results in the formation of pigments which have excellent light stability. A further advantage is the resistance to leaching or bleeding in the presence of water. This may be encountered, for example, in handling the prints, where moisture from the hands may cause the image to run or smear or offset onto the hands. It can also be a problem when a water-based overcoating solution is used to provide a protective overcoat for the finished print. Such overcoats could be gelatin or poly(vinyl alcohol) for example.

One facet of this invention is the formation of colorants having improved light stability. This resistance to fading is determined in accordance with a stimulated average north skylight (SANS) test. In this test, samples bearing an image comprising the pigments of this invention are subjected to the output of a xenon source the spectral distribution of which closely approximates that of the average light from the north sky. The samples are prepared by forming on a suitable charge-retaining material an electrostatic charge pattern corresponding to a step-tablet exposure. The charge pattern is developed by solid-area development techniques utilizing a developer prepared as described below and containing pigments of the invention. A colored image corresponding to the original step tablet is obtained upon such development. The illuminance of the light from the average north sky on a vertical surface is approximately 250 foot-candles, while that from a xenon source under the conditions of the test is approximately 500 foot-candles. The test thus subjects the sample to conditions of fading about twice as severe as would be encountered outdoors out of the direct sunlight. The amount of fading is expressed in terms of the ratio of the loss in optical density (D), as defined hereinafter, to the optical density of the same area of the sample prior to the fading test. It is commonly expressed as a percentage loss.

The effectiveness of the present pigments as light absorbers is determined spectrophotometrically. A small amount of the pigment is mixed in a container with a suitable liquid which has a very slight solvent action upon it. When the solution is saturated, as indicated by undissolved pigment settling to the bottom of the container, a small amount is poured into a photometric cell. The cell is bounded on two opposite parallel faces by quartz windows, in order that both visible and ultraviolet light may pass through without attenuation. Such a cell is constructed with a predetermined distance between the inner surfaces of the transparent faces, such as, for example, 0.5 cm or 1.0 cm. After filling the cell with the solution, it is placed in the beam of a recording spectrophotometer, which is calibrated to automatically plot a con-

tinuous curve of transmittance (T) or optical density (D) as a function of wavelength. Optical transmittance is the ratio of the intensity of radiation transmitted by the sample to the intensity incident on the sample. It is expressed either as a percent (e.g., 75%) or decimal (e.g., 0.75). The optical density is defined in accordance with the following formula:

$$D = \log_{10} (1/T)$$

and is expressed as a decimal. The density is customarily read at the point on the curve at which it is a maximum, that is, at which the transmittance is a minimum, and the wavelength specified. The solvent used, the concentration of the pigment in the solution, and the inside thickness of the cell used are also customarily specified.

The pigments of the present invention can be used to prepare electroscopic toners. Dry toners can be prepared by various methods. Two convenient techniques for preparing these toners are spray-drying or melt-blending followed by grinding. Spray-drying involves dissolving the polymer, colorant and viscosity modifying agent in a volatile organic solvent such as dimethylformamide or dimethylsulfoxide. This solution is then sprayed through an atomizing nozzle using a substantially non-reactive gas such as nitrogen as the atomizing agent. During atomization, the volatile solvent evaporates from the airborne droplets, producing toner particles of the uniformly dyed resin. The ultrasonic particle size is determined by varying the size of the atomizing nozzle and the pressure of the gaseous atomizing agent. Conventionally, particles of a diameter between $\frac{1}{2}\mu$ and 25μ are used, with particles between 5μ and 15μ being preferred, although larger particles can be used when desired for particular development conditions or developer compositions.

Toners containing the present pigments can also be prepared by melt-blending. This technique involves melting a powdered form of polymer or resin and mixing it with the pigments and any other desired additives. The resin can readily be melted on heated compounding rolls which are also useful to stir or otherwise blend the resin and addenda so as to promote the complete intermixing of these various ingredients. After thorough blending, the mixture is cooled and solidified. The resultant solid mass is then broken into small pieces and finely ground to form a free flowing powder of toner particles. The resultant toner particles usually range in size from $\frac{1}{2}$ to 25μ .

After preparation, the toner is intimately mixed with a granular carrier vehicle to form a triboelectric developer composition. Carrier vehicles which can be used with the present toners to form new developer compositions

can be selected from a variety of materials. Suitable carriers useful in this invention include various non-magnetic particles such as glass beads, crystals of inorganic salts such as sodium or potassium chloride, hard resin particles, or metal particles. In addition, magnetic carrier particles can be used in connection with this invention. Suitable magnetic carrier materials are particles comprising such ferromagnetic materials as iron, cobalt, nickel and alloys thereof. Such particles may comprise a low-density non-magnetic core such as a resin or glass bearing a thin, continuous coating of a ferromagnetic material. They may equally comprise a magnetic (e.g., iron) core material bearing a thin, continuous layer of an electrically conducting metal having a resistance to aerial oxidation greater than that of iron, as disclosed in copending application No. 6844/70 (Specification No. 1303267). If desired, such metallic core particles may be acid washed prior to coating to improve the surface conductivity and adhesion of the coating as described in copending application No. 6843/70 (Specification No. 1303845). Still other useful magnetic carriers are ferromagnetic particles overcoated with a thin, continuous layer of a film-forming, alkali-soluble carboxylated polymer as disclosed in copending application No. 4867/69 (Specification No. 1251752). Carrier particles usually range in size from 1200 to 40 microns average diameter. Particularly useful results are obtained using particles of from 600 to 60 microns average diameter. The phrase "average diameter" as used herein is not meant to imply that only perfectly uniformly dimensioned particles can be used. This phrase is used to generally refer to the average thickness of particles when measured along several axes. Average diameter or particle size also refers generally to the approximate size of the openings in a standard sieve which will just retain or just pass a given particle.

Useful liquid developers can be prepared by simply dispersing the pigments in an insulating carrier liquid. Carrier liquids which may be used to form such developers can be selected from a wide variety of materials. Preferably, the liquid has a low dielectric constant and a very high electrical resistance such that it will not disturb or destroy the electrostatic latent image. In general, useful carrier liquids should have a dielectric constant of less than 3, should have a volume resistivity of greater than 10^6 ohm-cm and should be stable under a variety of conditions. Suitable carrier liquids include halogenated hydrocarbon solvents, for example, fluorinated lower alkanes, such as trichloromonofluoromethane or trichlorotifluoromethane having a boiling range of from 2°C to 55°C. Other hydrocarbon solvents are useful such as isoparaffinic hydrocarbons having a boiling range of from 145°C to 185°C such as Isopar C (Humble Oil & Refining Co.) or cyclohydrocarbons such as cyclohexane. Additional useful carrier liquids include polysiloxanes, odorless mineral spirits and octane.

In addition to containing the colorants of the present invention, preferred developers also contain a resinous material to facilitate binding of the colorant to the surface to be developed. Suitable resinous materials used in the present developers appear to form a coating around each colorant particle and thus also facilitate dispersion of the colorants in the carrier liquid. Useful resins can be selected from a wide variety of substances. The following are illustrative of suitable materials; rosins, including hydrogenated rosins and esters of hydrogenated rosins, alkyl methacrylate copolymers having from 2 to 5 carbon atoms in each alkyl moiety, such as isobutyl methacrylate and normal butyl methacrylate copolymers; phenolic resins, including modified phenolic resins such as phenol formaldehyde resins; pentaerythritol phthalate; coumarone-indene resins; ester gum resins; vegetable oil polyamides; polycarbonates; alkyd resins, including modified alkyds such as soya oil-modified and linseed oil modified alkyds, and phthalic, maleic and styrenated alkyds.

Developers containing suitable binders are conveniently prepared by solvent milling. A quantity of a suitable polymer or polymers to be used as the binder is dissolved in a mild solvent and placed in a ball mill. The present pigments are added to the mix and the combination is milled for a suitable time, typically up to a week. Alternatively, the resin may be dissolved alone initially, and placed on compounding rolls in the manner described in connection with the preparation of dry toners. The pigments and other ingredients are then added on the mill. In either case, milling is often done in the presence of the final carrier liquid or a liquid mutually soluble in it in order that resin, pigment and carrier may become thoroughly mixed. After milling is completed, the concentrate is diluted to working strength by thoroughly blending it with a suitable electrically insulating carrier liquid. The resultant developer is in the form of a carrier liquid having dispersed therein toner particles comprised of the pigments of this invention and a resinous binder material.

In addition, the polarity of electrostatic charge of the liquid developer compositions of the present invention can be enhanced or altered by the addition of suitable charge control agents if so desired. A variety of materials can be used as charge control agents. Illustrative of suitable charge agents would be the polyoxyethylated alkyl surfactants such as polyoxyethylated alkylamine, polyoxyethylene palmitate a polyoxyethylene

stearate. Other useful materials are magnesium and heavier metal soaps of fatty and aromatic acids as described in U.S. Patent No. 3,417,019. Useful metal soaps include 5 cobalt naphthenate, magnesium naphthenate and manganese naphthenate, zinc resinate, calcium naphthenate, zinc linoleate, aluminum resinate, isopropyl-titanium stearate, aluminum stearate, and others, many of which 10 are also described in U.S. Patent No. 3,259,581. Typically, the amount of such materials used is less than 2% by weight based on the weight of toner. In certain 15 instances, the resinous binder per se can function as the charge control agent as can the colorant.

As mentioned above, suitable developer 20 compositions can be prepared simply by grinding the pigments to the appropriate size and dispersing the pigment powder in a carrier liquid without the addition of a resinous binder and/or charge control agent. A developer which does not contain a binder material would produce developed images 25 which were not fixed. Accordingly, it would be necessary to overcoat such images by spraying with a lacquer composition in order to hold the pigment particles in place.

The pigment particles of the present 30 invention generally have an average particle size of from 0.05 to 5μ , with preferred materials in the range of from 0.1 to 1 micron. Typical liquid developer compositions of 35 this invention will contain the present pigments in a concentration of from 0.01 to 1.0 gram per litre. When a resin binder is used, the pigment to binder weight ratio can vary from 1:20 to 2:1.

The toner and developer compositions of 40 this invention can be used in a variety of ways to develop electrostatic charge patterns. Such developable charge patterns can be prepared by a number of means and can be carried on either an electrophotographic material 45 or on a non-sensitive material such as an electrically insulating receiver sheet as well known in the art.

The following Examples are included for 50 a further understanding of the invention.

Example 1

A 50 gram portion of the basic yellow dye Genacryl Yellow 5 GF (C. I. Basic Yellow 13) is dissolved in 1250 ml. of hot water (95°C) with stirring. The solution is filtered 55 to remove undissolved material and cooled to 60°C. A 28 gram portion of the acidic dye Xylene Light Yellow N2G (C. I. 18965, Acid Yellow 17) is dissolved in 700 ml. of hot water as above with stirring, and the solution 60 filtered and cooled. The solution of acidic dye is then slowly added to the solution of basic dye with rapid stirring, producing a yellow precipitate. A 30 gram portion of phosphotungstic acid is dissolved in 500 ml. of

water, and the solution added to the suspension of pigment. The suspension of pigment thickens to a slurry. The container is heated until the water temperature reaches about 90°C, at which point 250 grams of anhydrous sodium acetate are added and the suspension stirred for an additional 15 minutes. The suspension is allowed to stand until the water reaches room temperature (about 20°C), after which the suspension of pigment is filtered off and pressed dry on a Büchner funnel. The cake is extracted in turn in 2500 ml. of cold water, a mixture of 1500 ml. of ethyl acetate and 200 ml. of isopropyl alcohol, and finally 800 ml. of ethylene acetate, being filtered and pressed dry after each extraction. The pigment is dried on a steam bath for about 15 hours to yield 27 grams of colorant. The maximum optical density of an ethanol solution of the pigment measured in accordance with the procedure previously given is 1.43 at a wavelength of 408 nm. The density is measured at a solution concentration of 1 part of pigment per 25,000 parts of ethanol, at a cell thickness of 1.0 cm. In order to form a developer, liquid concentrate is first prepared by combining the following materials and ball milling them for a period of about 7 days.

Pigment	1 g.	95
Phenol-formaldehyde resin	3 g.	
Soya oil-modified phthalic alkyd resin	1 g.	
Solvent	15 ml.	

After ball milling, the particle size of the resultant material is from 1 to 5 microns. The solvent used is a cyclohydrocarbon having a major aromatic component and having a boiling range of from about 300 to 360°F (Solvesso 100, Humble Oil & Refining Co.). Two and a half grams of the above concentrate are added dropwise to 250 ml. of an electrically insulating carrier liquid which is comprised of an isoparaffinic hydrocarbon having a boiling range of from 300 to 360°F (Isopar G, Humble Oil & Refining Co.) containing 0.2 grams of cobalt naphthenate and 0.45 grams of 1.5% solution of aluminum stearate in xylene. The resultant mixture is vigorously agitated for 3 minutes after the addition of all the concentrate. The resultant developer is then used to develop an electrostatic charge pattern carried on an electrophotographic material comprised of a poly(ethylene terephthalate) film base having an electrically conductive substrate which is overcoated with a photoconductive layer comprising an organic photoconductor and a polycarbonate resin binder. The pattern is produced by uniformly charging and exposing it through a transmission stepped density gray scale. The electrostatic image thus produced is developed by contacting it with the

developer in the presence of a closely spaced development electrode to give solid-area development, as is well known in the art. The image thus prepared is subjected to the SANS test, previously described, for 28 days. The image undergoes no loss in density, while a control image prepared from a developer containing a pigment prepared in the same way except that the phosphotungstic acid treatment was omitted has an optical density one-half of that made from the phosphotungstic acid treatment. The developer of this Example gives an image which has excellent resistance to smudging due to handling.

Example 2

An 11.7 gram portion of the acidic dye Xylene Red B (C. I. 45100) is dissolved in one liter of water at a temperature of 95°C. A 10 gram portion of the basic dye Rhodamine B (C. I. 45170) is dissolved in another one liter portion of hot water. The latter solution is slowly added, with stirring, to the solution of the acidic dye, producing a thick slurry. Stirring is continued for 15 minutes while the slurry is allowed to cool to room temperature. It is then filtered and pressed dry. The pigment is stirred up again with two liters of cold water for 10 minutes, filtered, and pressed dry. It is stirred up with one liter of hot ethyl acetate for 10 minutes and filtered, extracted with 500 ml. of cold ethyl acetate, and finally washed down on the filter with 300 ml. of acetone and dried on a steam bath for 1 hour. The yield of product is 7.3 grams. The optical density of an ethanol solution of the pigment at a concentration of 1:125,000 is 1.28, at a wavelength of 548 nm. The thickness of the sample cell is 1.0 cm. Another pigment is made in the same way except that the slurry is treated with phosphotungstic acid as in Example 1 prior to isolation of the pigment from the solution. Developers are made from both pigments as in Example 1, from which gray scale images are prepared as described in Example 1. The image made from the developer containing the pigment prepared in the presence of the phosphotungstic acid lost only 5% density in a 28 day SANS test while the image prepared from the developer containing pigment prepared in the absence of the phosphotungstic acid lost approximately 25% of its original density. Clearly, the treatment with phosphotungstic acid has greatly improved the stability of the pigment to light fading.

Example 3

The procedure of Example 1 is followed substituting the magenta dye Xylene Red B (C. I. 45100) for the acidic yellow dye indicated there, and substituting Astraphloxine FF (C. I. 48070) for the basic dye used in that Example. An electrophotographic liquid developer made as in Example 1 is used to develop an electrostatic charge pattern resulting from exposure to a gray scale, also as in Example 1. A control developer is made from a pigment made in this manner except that the phosphotungstic acid treatment of the pigment is omitted. It is also used to develop a similarly made electrostatic charge pattern. Good images are obtained in both instances. Fading tests according to the SANS conditions given above show that the developer containing the treated pigment gives images which lose only about 5% of their original density after 28 days, while the developer containing the untreated pigment gives images which lose nearly 25% of their original density after the same period of time.

Example 4

A 5.8 gram portion of the acidic dye Xylene Red B (C. I. 45100) is dissolved in 150 ml. of hot water and cooled to 60°C. A solution of 4.8 grams of the basic dye Rhodamine B (C. I. 45170) dissolved in 250 ml. of hot water and cooled to 60°C is added with stirring. Complete precipitation results with formation of a sticky mass, and upon cooling to room temperature the pigment solidifies and is broken to a powder by stirring. The pigment is filtered, stirred with 300 ml. of water at room temperature, filtered, and pressed dry. It is then stirred with 300 ml. of ethyl acetate for 10 minutes, filtered, pressed dry, and dried on a steam bath to yield 7.3 grams of product. A test patch image prepared from this pigment underwent a change in optical density of from 1.07 to 0.46 in a 28 day SANS test, which represents a density loss of 57 percent. A second pigment is prepared in the same manner except that the dye solutions are cooled to room temperature before mixing, resulting in a fine powdery precipitate, and 6.0 g. of phosphotungstic acid in 300 ml. of water is immediately added. Stirring is continued for one half hour and the pigment is filtered, stirred with 500 ml. of cold water for 20 minutes, filtered, and pressed dry. It is then extracted with two 300 ml. portions of hot ethyl acetate, filtered, pressed dry, and dried on a steam bath to yield 5.1 grams of product. A test patch image prepared from this pigment underwent a change in optical density of from 1.09 to 0.88 in a 28 day SANS test, which represents a density loss of 19.3 percent. A third pigment was prepared in the same manner as the second pigment except that 6.0 g. of phosphomolybdc acid was used in place of the 6.0 g. of phosphotungstic acid and the yield of product was 9.3 grams. A test patch image prepared from this pigment underwent a change in optical density of from 0.80 to 0.52 in a 28 day SANS test, which represents a density loss of 35 percent. This example demonstrates that treat-

ing the precipitate formed by reaction of the acidic dye with the basic dye with either phosphotungstic acid or phosphomolybdic acid substantially improves its light stability.

5 The dyes mentioned specifically herein are only illustrative of the invention and are not meant to be limiting as virtually any acidic dyes and basic dyes of the types defined herein are useful provided the particular materials selected are capable of precipitating with one another. Similarly, the particular resins and insulating carrier liquids mentioned are merely illustrative of the many such useful materials found in the art of electro-photography.

10 "Isopar" and "Solvesso" are registered Trade Marks.

15 **WHAT WE CLAIM IS:—**

20 1. A process for the formation of a pigment comprising the steps of reacting in an aqueous medium an acidic dye (or a salt thereof) which is water-soluble and has an acidity such that a saturated aqueous solution thereof has a pH less than 5, with a basic dye (or a salt thereof) which is also water-soluble and has a basicity such that a saturated aqueous solution thereof has a pH greater than 8, so as to form a precipitate and then treating the precipitate with an acidic mordant.

25 2. A process as claimed in Claim 1, in which the acidic mordant is phosphotungstic acid, phosphomolybdic acid or a mixture thereof.

30 3. A process as claimed in Claim 1 or 2, in which the acidic dye contains at least two sulphonic or carboxylic groups per molecule.

35 4. A process as claimed in Claim 3, in which the acidic dye is a nitro, azo, aryl-

methane, methine, acridine, thiazole, azine, anthraquinone or phthalocyanine dye.

5. A process as claimed in any of Claims 1 to 4, in which the basic dye contains at least two amino groups per molecule.

6. A process as claimed in Claim 5, in which the basic dye is a nitro, azo, arylmethane, methine, acridine, thiazole, azine, anthraquinone or phthalocyanine dye.

7. A process as claimed in Claim 1 for the formation of a pigment comprising the steps of reacting an acidic dye with a basic dye so as to form a precipitate and then treating the precipitate with an acidic mordant, substantially as described in any one of the Examples herein.

8. A pigment whenever produced by a process as claimed in any one of the preceding claims.

9. An electrophotographic developer which is either a dry composition comprising carrier particles and marking particles or a liquid composition comprising a carrier liquid having dispersed therein marking particles, wherein the marking particles comprise a pigment as claimed in Claim 8.

10. An electrophotographic developer as claimed in Claim 9, in which the marking particles further comprise a resin binder.

11. An electrophotographic developer as claimed in Claim 9, substantially as described in any one of Examples 1 to 3 herein.

12. A process of developing an electrostatic charge pattern which comprises contacting the charge pattern with an electrophotographic developer as claimed in any of Claims 9 to 11.

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